

**FINAL REPORT
AMORPHOUS SEMICONDUCTORS**

10 June 1964 to 2 August 1967

Contract No. NASW-934
Melpar Job No. 4276

Submitted to

National Aeronautics & Space Administration
Office of Electrophysics Programs
Washington, D.C. 20546

Submitted by

Melpar, Inc.
7700 Arlington Boulevard
Falls Church, Virginia 22046

TABLE OF CONTENTS

	<u>Page</u>
1. INTRODUCTION	1
2. TECHNICAL DISCUSSION	1
2.1 Optical Properties of Amorphous Semiconductors	1
2.2 The Electrical Properties of Boron Layers	13
2.2.1 Introduction	13
2.2.2 Negative Resistance and Switching	15
2.2.3 Electron Energy Levels in Boron	15
2.2.4 Conduction Mechanism	15
2.3 References	16
3. PUBLICATIONS	18
4. PERSONNEL	18
5. SUMMARY	19
APPENDIX: Switching and Negative Resistance in Amorphous Boron Layers	20

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Absorption of Crystalline (I) and Amorphous (II) Germanium Thin-Films	3
2	Absorption of Thin Deposited Silicon Films: I Polycrystalline, II Amorphous	4
3	Energy vs Absorption Coefficient for Amorphous Boron Film	6
4	Indirect (a) and Direct (b) Transition Regions for Boron Films	7
5	Index of Refraction vs Wavelength	8
6	Absorption Coefficient, α , of a Thin Boron Film as a Function of Energy	9
7	Log I_0/I vs Energy in Amorphous Boron Films	11

1. INTRODUCTION

This final report on amorphous semiconductors is submitted in compliance with Contract Number NASW-934 as amended and covers the period from 10 June 1964 to 2 August 1967. During this period, Melpar was engaged in the study of amorphous thin films and their electrical and optical properties. A number of semiconductor materials have been examined. These include selenium, germanium, silicon, and boron. As work progressed and as information was accumulated, a number of publications were prepared; these are listed in section 3.

The summary of our results on the optical properties of amorphous semiconductors appears in section 2.1, while the summary of the electrical properties appears in section 2.2.

During the first year of this contract, a large amount of work was done on selenium films of various thicknesses using a contactless inductor technique to determine changes in electrical conductivity with temperature while eliminating any contact problems. Early in the year, work on another contract indicated that thin films of boron would be a fruitful field for further study. As a result, much of the effort expended during the last 2-1/2 years was in the study of amorphous thin films of boron. These studies involved electrical and optical studies. Various electrical measurements were made from 78°K to 500°K. Optical absorption measurements were made over the range of 1200 Å to 16μ, while reflection measurements were made from 2000Å to 16μ.

In the course of the work, a number of avenues were investigated to provide confirmation of theory or to better understand the experimental results.

The work done on molecular association in boron vapor, the coordination number in amorphous boron and germanium, the dispersion of amorphous boron thin films, and infrared absorption in high-purity boron films, would fall in this category.

2. TECHNICAL DISCUSSION

The two major subject areas which were covered under this program have been the optical and electrical properties of amorphous thin films. A summary of the findings in these two fields appears in the succeeding sections and in the appendix to this report.

2.1 Optical Properties of Amorphous Semiconductors

In this section we discuss the optical absorption in amorphous germanium, silicon, and boron. These are the amorphous semiconductors studied during the tenure of the present contract. For completion, we include a brief discussion of work done on amorphous germanium and a few other semiconductors which have been under study at other laboratories.

Our results on amorphous films of germanium, silicon, and boron have been previously reported in quarterly report numbers 6, 7, 8, and 10. Here an attempt is made to correlate these results with the changes that appear in the band structure as one goes from a crystalline to the amorphous state. Furthermore, our results on the infrared absorption spectrum of amorphous boron¹ throw light on the existence of impurity levels in amorphous substances.

Since the band structure and the optical properties of crystalline germanium and silicon are now fairly well understood,² it is much easier to discuss and correlate the changes that appear in these substances when the long range order is destroyed. Therefore, we first start with the description of the properties of amorphous germanium and silicon. Apart from the work carried out in our laboratory, amorphous germanium has also been studied optically by Tauc et al.³ and Clark.⁴ The optical absorption curves for amorphous films of germanium and silicon in the energy range 2 eV to 6 eV (i. e., above the fundamental absorption edge) are shown in figures 1 and 2. For comparison, we also include similar curves for polycrystalline films. The method for obtaining these curves has been discussed in the 7th quarterly report.

While polycrystalline films of germanium, in the region above the fundamental absorption edge, have been previously studied,^{5, 6} to the best of our knowledge this is the first time that well-crystallized and very thin samples of silicon have been subjected to detailed transmission measurements. For both substances, the structure exhibited in the absorption curves for polycrystalline films are in good agreement with the absorption data obtained from reflection studies on single crystals.⁷ As is well known,² this structure is connected with the direct transitions (i. e., transitions where both energy E and the crystal momentum \vec{k} are conserved) at the critical points in the Brillouin zone. That is, points at which the joint-density-of-states function has singularities.

We notice that for amorphous films of germanium and silicon, this structure is completely smeared out and for both substances, one obtains a broad absorption band instead. For germanium, Tauc et al.^{3a} have also reported the same effect. One concludes that all transitions between the lowermost valence band and the uppermost conduction band in amorphous germanium and silicon are indirect, i. e., the \vec{k} -selection rule breaks down. Further quantitative support for this conclusion is obtained from the data of Tauc et al.^{3b} on amorphous germanium in the region of the fundamental absorption edge 0.7 eV to 1.7 eV. Their data fit the expression for indirect transitions (i. e., $\omega^2 \epsilon_2 \propto (\hbar\omega - E_g)^2$, where $\hbar\omega$ is the energy of the incident photon; ϵ_2 , the imaginary part of the dielectric constant, and E_g , the band gap) with $E_g = 0.88$ eV, showing no appreciable change from the value of the band gap in crystalline germanium.

It should be pointed out that in the above region, Tauc et al. also observe a broad peak situated at 0.86 eV. Such a peak doesn't appear either in our experiments or in those of Clark.⁴ Tauc et al. ascribe this peak to excitons bound to neutral acceptors.

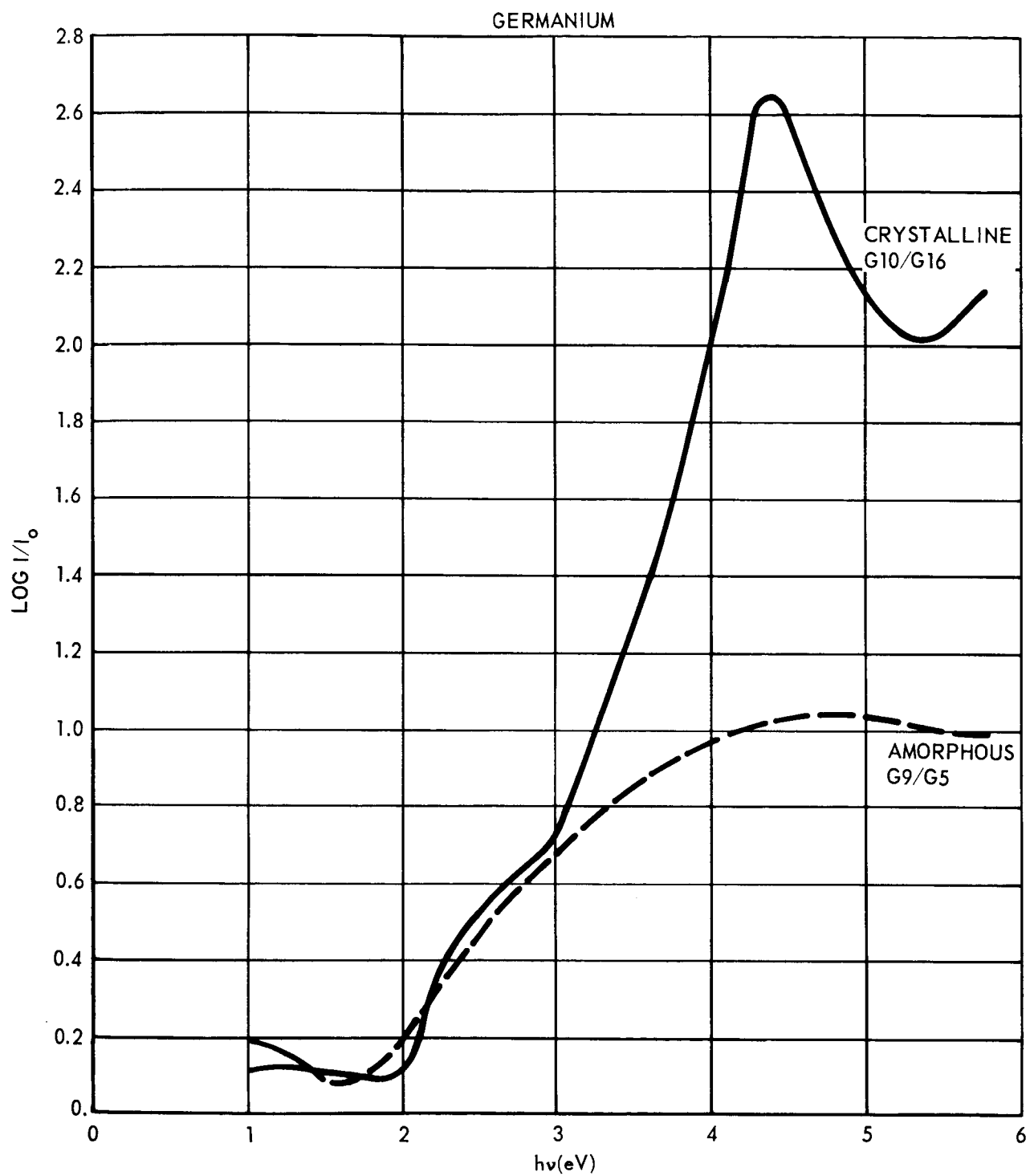


Figure 1. Absorption of Crystalline (I) and Amorphous (II) Germanium Thin Films

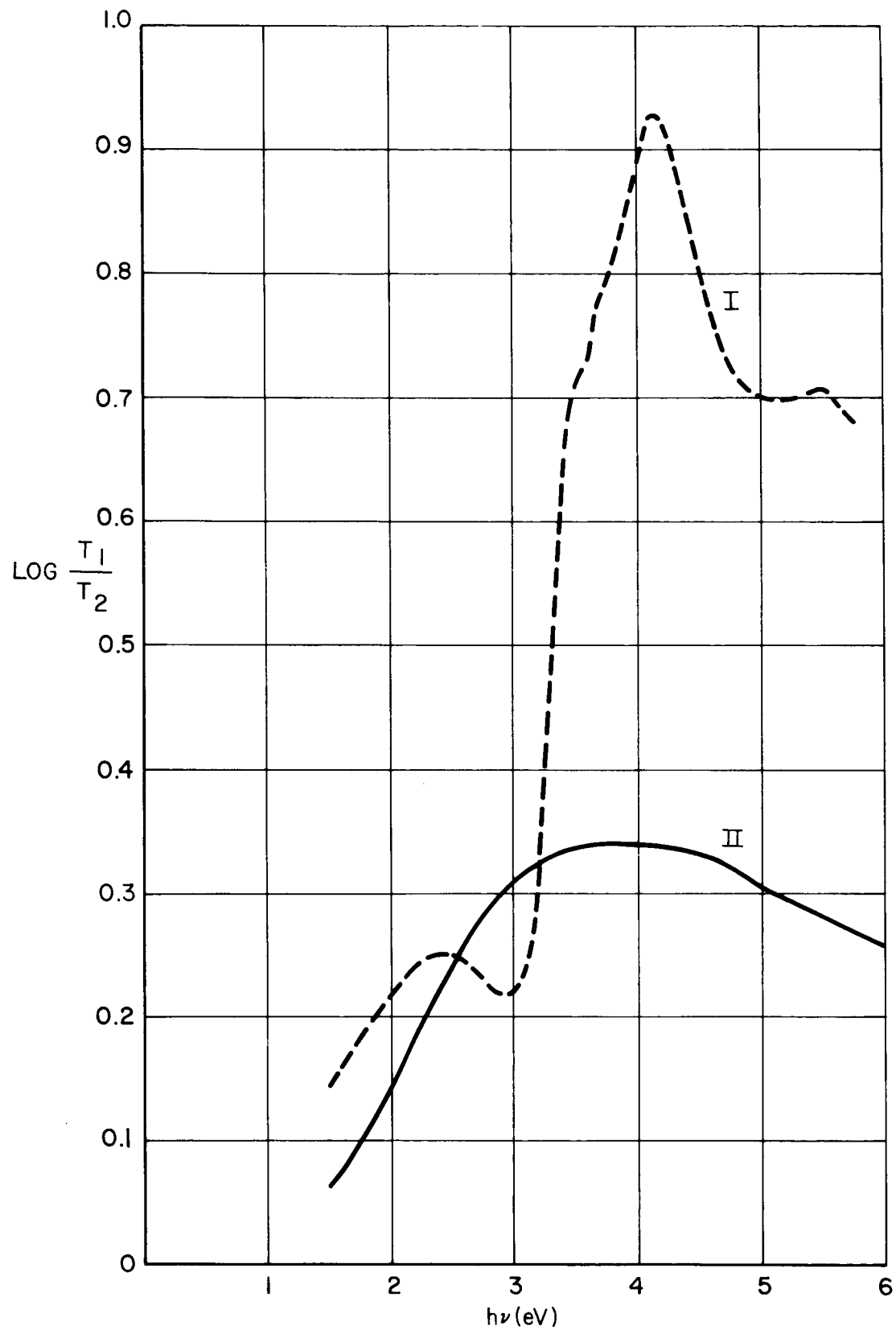


Figure 2. Absorption of Thin Deposited Silicon Films: I Polycrystalline, II Amorphous

What is very interesting and somewhat surprising is the absorption data^{3b} on amorphous germanium in the infrared region 0.1 eV to 0.5 eV. For crystalline germanium, in this region, there are direct transitions (i.e., \vec{k} -conserving) from the lower branch of the valence band to the two upper branches. It is found^{3b} that these transitions retain their \vec{k} -conserving character in the amorphous state. This indicates that the valence band wave functions are well described by Bloch functions, even in the amorphous state.

The case of boron is far more difficult to discuss quantitatively, since for all practical purposes the band structure of boron still remains unknown. This is, of course, due to the large number of atoms per unit cell in boron. Many groups^{8,9} have studied optical absorption in crystalline boron but most studies are confined to the region of fundamental absorption edge except that of Gaule *et al.*⁹ whose data extend to about 3.6 eV. We have studied amorphous boron from the far infrared to the extreme ultraviolet (0.07 eV to 9.0 eV) and our results are discussed below.

The most quantitative analysis for crystalline boron in the region of fundamental absorption edge is that of Dhamagidze *et al.*⁸ who find that in the region 0.8 to 1.45 eV, the indirect transitions between the valence and the conduction band are important while direct transitions dominate in the region 1.45 eV to 1.7 eV. This shows that the top of the valence band and the bottom of the conduction band lie at different points in the Brillouin zone. The values of the band gaps are found to be $E_g^{\text{indirect}} = 0.93$ eV with the associated phonon energy $E_{\text{phonon}} = 0.16$ eV and $E_g^{\text{direct}} = 1.47$ eV. The other reported values for E_g^{direct} of crystalline boron are 1.53 eV (Dietz and Herrmann), 1.41 eV to 1.44 eV (Brungs), 1.26 eV (Gebhart and Jacobsmeier) and 1.55 eV (Gaule, Breslin, and Patty).

In the sixth quarterly report, we carried out an analysis of the absorption coefficient α of an amorphous boron film of thickness 1.13 micron (figure 3). It was found that indirect and direct transitions maintain their identity in their respective energy ranges 0.8 eV to 1.4 eV and 1.45 eV to 1.8 eV. Moreover, the values of the band gaps, $E_g^{\text{indirect}} = 0.92$ eV and $E_g^{\text{direct}} = 1.44$ eV (figure 4) are extremely close to those reported by Dhamagidze *et al.*⁸ for crystalline boron. In our work, we assumed the constant value 0.29 for the reflection coefficient of boron in order to facilitate comparison with the data of Dhamagidze *et al.*, who made the same assumption. This is certainly not entirely justified, but our data on the refractive index of boron (figure 5) shows that the reflection coefficient changes only slightly in this region (from 0.27 at 0.8 eV to 0.29 at 1.5 eV). Thus, if the above assumption is justified, one tends to conclude that the band structure of boron goes through only nominal change as one goes from ordered to the disordered state.

It must, however, be pointed out that as reported in the 7th quarterly report, a novel method used to eliminate reflection correction leads to an absorption curve for amorphous boron (figure 6) which differs considerably from the one discussed above. It doesn't fit direct or indirect, forbidden or allowed transitions. The measurements

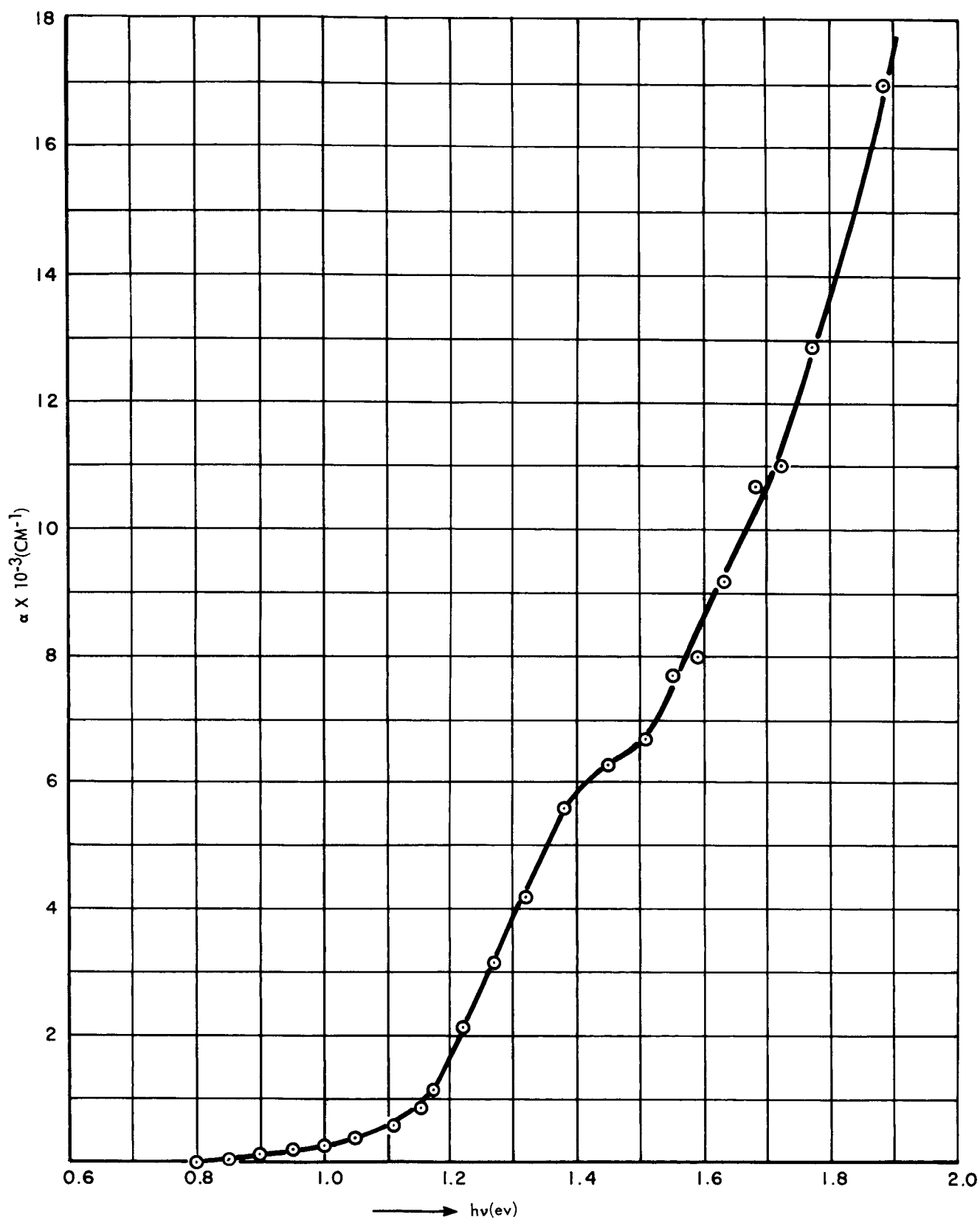


Figure 3. Energy vs. Absorption Coefficient for Amorphous Boron Film

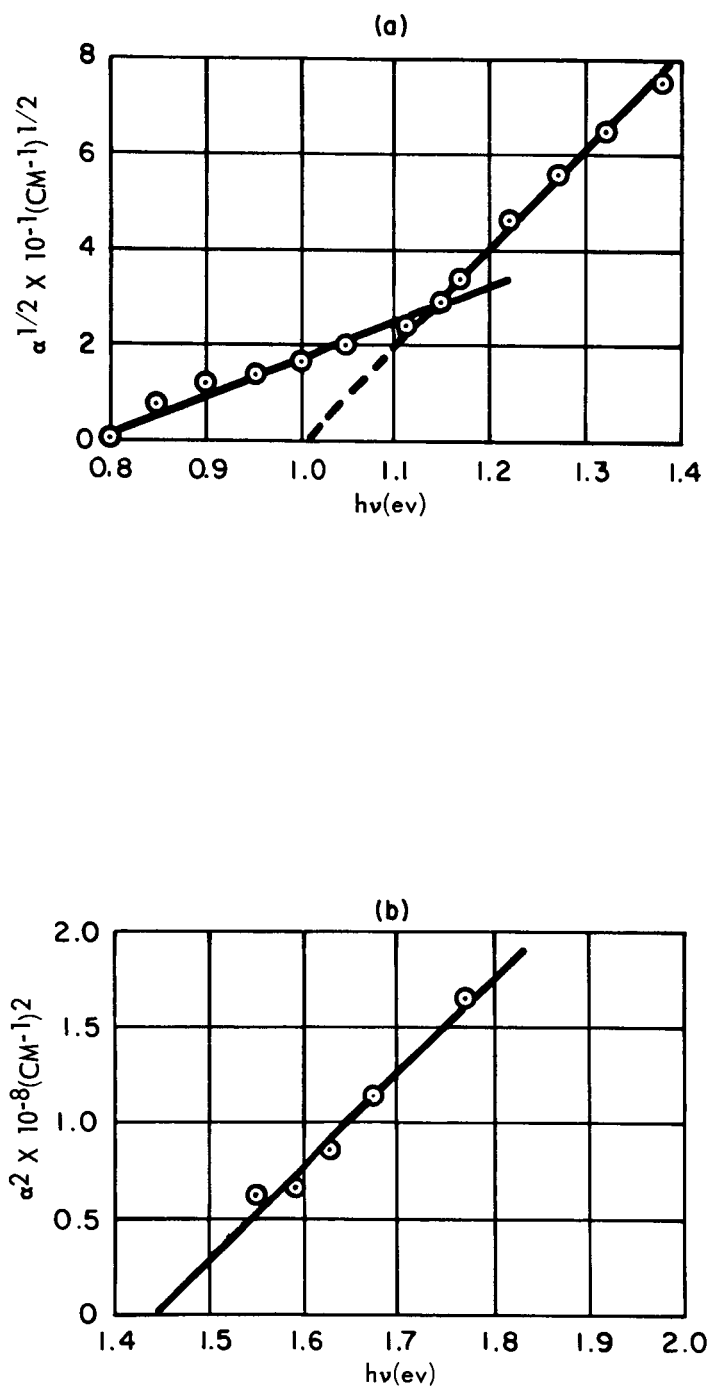


Figure 4. Indirect (a) and Direct (b) Transition Regions for Boron Films

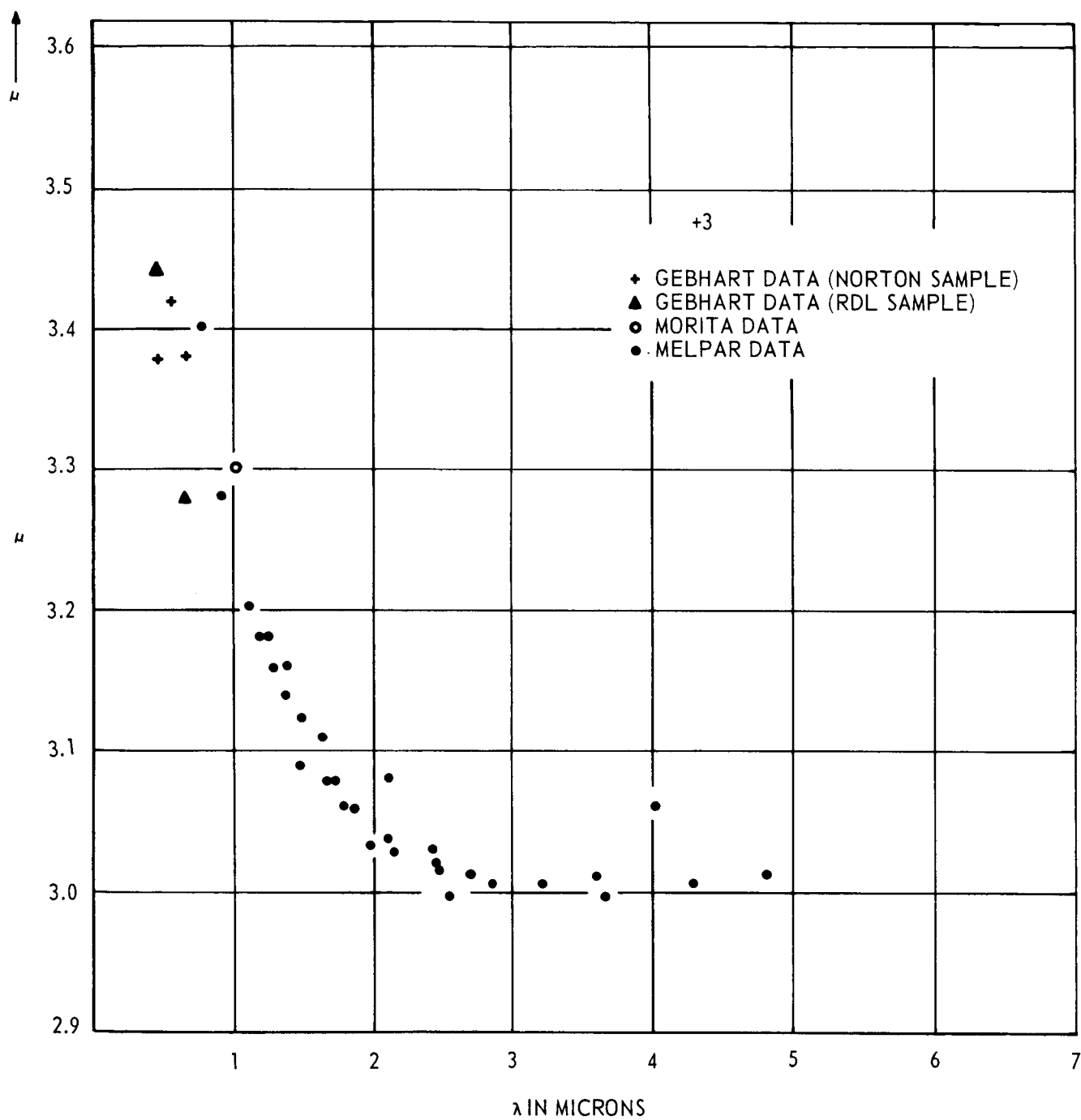


Figure 5. Index of Refraction vs. Wavelength



Figure 6. Absorption Coefficient, α , of a Thin Boron Film as a Function of Energy

reported in the 7th quarterly report were extended in energy up to 4.2 eV and revealed a minimum in absorption at 2.55 eV beyond which the absorption increased again. Such a minimum has been reported by Gaulé et al.⁹ for crystalline boron at approximately the same energy and must correspond to an onset of a new transition at some other point (other than that associated with the fundamental absorption edge) in the Brillouin zone. This minimum has been repeatedly observed in our experiments. Even the values of the absorption coefficient are quite similar for the crystalline ($\alpha = 3 \times 10^4 \text{ cm}^{-1}$) and the amorphous ($\alpha = 4 \times 10^4 \text{ cm}^{-1}$) states of boron. But beyond the minimum, the absorption coefficient rises much more rapidly in the amorphous form than in the crystalline form. The retention of this structure in the amorphous state leaves little doubt that the band structure of boron does not change appreciably at energies higher than those associated with the fundamental absorption edge.

As remarked above, the crystalline boron has only been studied up to 3.6 eV. The retention of the minimum at 2.55 eV in amorphous boron encouraged us to study amorphous films of boron at energies beyond 3.6 eV to investigate if any structure exists at higher energies. The transmission curve of a 100 Å thick boron film deposited on LiF covering the energy range 5.2 eV to 9.0 eV is shown in figure 7. The curve was obtained utilizing the extreme ultraviolet spectrophotometer (Romand-Vodar type) at the Laboratoire des Hautes Pressions, CNRS, Bellevue-92, France. As shown, the absorption (proportional to $\log \frac{I_0}{I}$) increases from 5.2 eV to 9.0 eV without exhibiting any structure.

One of the purposes of the present study was to check whether the impurities are active in amorphous substances (see original proposal). Our work on infrared absorption of amorphous boron films¹ indicates that impurity absorption definitely plays a role in this energy range and that the impurity levels are indeed optically active. Also, Stuke¹⁰ finds that, electrically, the impurities are just as active in amorphous tellurium as in crystalline tellurium.

To summarize, our optical results on amorphous boron studied from far infrared to the extreme ultraviolet region (0.07 eV to 9.0 eV) indicate that the band structure of boron is not very much modified and the impurity levels do play a role in the amorphous state. As discussed above, the conclusion regarding non-modification of the band structure (including the band gap) holds true for germanium also. This is perhaps connected with the fact that the coordination number in amorphous forms of boron¹¹ and germanium¹² doesn't change appreciably from that in the crystalline form. However, for tellurium, which also retains its coordination number in the amorphous state, Stuke¹⁰ has reported a widening of the band gap by 0.4 eV.

If the above conclusions are correct, one would have to rule out the appearance of localized levels in the forbidden energy gap when one goes to the disordered (amorphous) state as has been proposed by Banyai¹³ in an attempt to explain the electrical

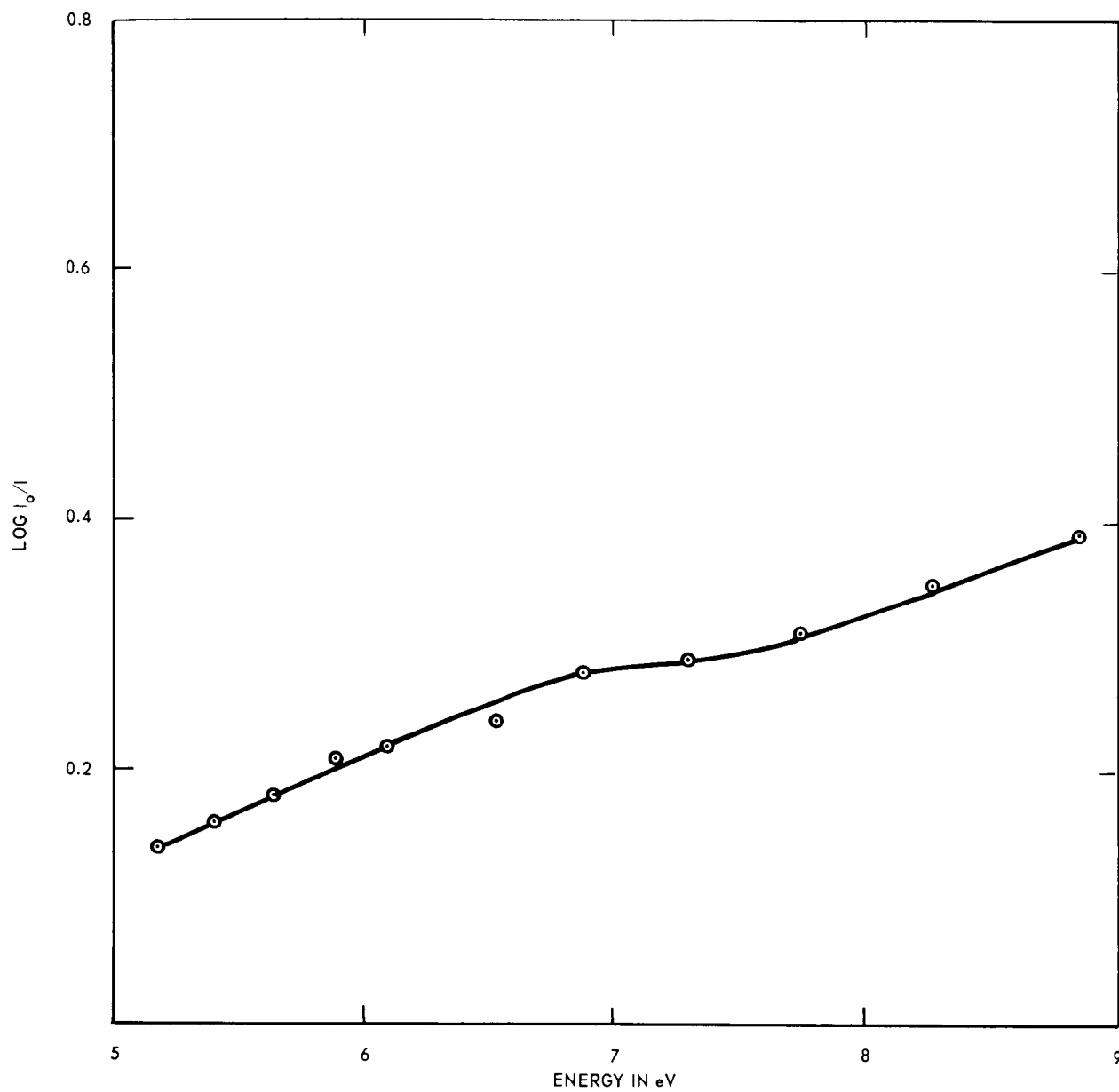


Figure 7. $\text{Log } I_0/I$ vs. Energy in Amorphous Boron Films

measurements on amorphous germanium.¹⁴ Another possible explanation of electric conduction in amorphous substances based on the existence of Schottky barriers has been discussed in the review article by Mott.¹⁰

Finally, we cite the interesting optical studies of Beaglehole¹⁵ on liquid xenon and Phillip¹⁶ on crystalline and fused quartz. It is found that unlike germanium and silicon, the structure observed in solid xenon¹⁷ and crystalline quartz is almost completely retained in the disordered forms of xenon (liquid) and quartz (amorphous), respectively. At least for the case of xenon, Roncin and Moorjani¹⁸ have argued that the structure is connected with atomic transitions rather than with the band structure and, therefore, not affected by the lack of long-range order in liquid xenon.

2.2 The Electrical Properties of Boron Layers

2.2.1 Introduction

During the course of this contract, progress has been made on understanding the electrical properties of amorphous semiconducting materials. Most of the experimental work has been carried out with boron. However, the electrical properties of amorphous silicon and germanium films appear to be similar. Nonlinear currents, switching, and negative resistance have been observed in silicon and germanium as well as boron. Boron is perhaps the least understood of all the elemental semiconductors and it is believed that concentrating on boron would be fruitful from many standpoints. Boron forms an amorphous, hard, durable film difficult to crystallize but which adheres well to glass substrates. It is now obtainable in a very pure form.

Because of its very high melting point ($\sim 2300^\circ\text{C}$), boron must be deposited with an electron beam. This is advantageous since it assures pure films. Boron reacts with most crucibles and filaments. Experiments to achieve the maximum purity by careful cleaning procedure coupled with residual gas analyses and IR spectra are discussed in Quarterly Report No. 6. It is thus possible to obtain high-purity layers of amorphous boron.

The boron layers exhibit an extremely high resistivity. Surface or planar electrodes of the type usually used for resistors could not be employed. It was possible to obtain reasonable currents by sandwiching the boron between two deposited metal electrodes. Electrodes such as gold, aluminum, and recently titanium have been used. Thermoelectric tests indicate "p"-type charge carriers. It was observed that currents through these films were nonlinear and obeyed a relation: (Quarterly Report No. 3.)

$$I = KV^n \quad (1)$$

where

I = current

V = voltage

n, K = constants $\neq n(V), K(V)$

Explanations for this very nonlinear behavior were hard to find. Initial experimental effort was placed on determining the relations of the constants K and n to various film parameters such as thickness, deposition rate, purity, resistivity, band gap, etc. (See Quarterly Report No. 3.) A direct experimental relation between n and K and other film parameters was not observed.

It was discovered, however, that, as the thickness of the sample increased the current also increased. This behavior was contrary to that expected in any type

of normal resistive material and indicated that carriers were being created somehow in the body of the material. A relation was found:

$$I = I_0 \exp (\alpha d) \quad (2)$$

where

d = thickness

$$\alpha = \alpha (E)$$

which held in every sample examined. This relation was interpreted as an avalanche process and α an ionization coefficient equal to the number of the new charge carriers produced per centimeter of material traversed. Plots of α versus field (E) were examined and given in Quarterly Report No. 3.

Since equations (1) and (2) describe the same phenomena (Quarterly Report No. 5) the quantities n and α are related by the following:

$$\alpha d = n \log_e (E/E_0) \quad (3)$$

where

E_0 = threshold for avalanche related to I_0

Research in the following years continued to confirm the multiplication process in amorphous films. Approximately 900 samples were examined during the course of this study.

Assuming the interpretation of the phenomena in terms of avalanche ionization, with a one-charge-carrier ionization coefficient α , $1/\alpha$ represents the average distance between ionizing collisions (ℓ_i). Using data given in the appendix, one finds at $E = 2.7 \times 10^5 \text{ V/cm}$:

$$\ell_i = \frac{1}{\alpha (E)} = 500 \text{ \AA} \quad (4)$$

Note this does not necessarily represent the mean free path of the carriers, but only the average path between ionizations. From Eq. (4) one may obtain the energy available for ionization (Q) at these collisions, thus:

$$Q = E \cdot \ell_i = 1.35 \text{ eV.}$$

This energy appears quite reasonable for creation of hole-electron pairs by collision. A common assumption is $Q = 3/2 E_g$. In this case, this gives $E_g = 0.9 \text{ eV}$ which is surprisingly close to that measured. (See appendix, table I.)

2.2.2 Negative Resistance and Switching

While examining the nonlinear current phenomena, a type of switching was occasionally observed. The current would suddenly become considerably larger than expected and a new stable, low resistance would follow. It was originally suspected that this was a filamentary type of breakdown in which conducting paths were formed through the material. The effect, however, persisted and seemed to be reversible. Effort was placed on this effect during the latter stages of the work (Quarterly Report No. 10). A change of electrode material from aluminum to titanium produced better switching characteristics. When aluminum was used, it was necessary to have some type of forming procedure in order to bring out a negative resistance. With titanium, negative resistance appeared immediately and was directly proportional to the area and thickness of the sample involved. Capacitance measurements indicated that the entire area was involved in the switching. Effort was spent in reviewing the literature and arriving at a reasonable explanation of the switching phenomena. These explanations were based on observations of the consistency of the switching voltages coupled with the avalanche ionization process. An explanation of the behavior was submitted for publication and is given in the appendix.

2.2.3 Electron Energy Levels in Boron

Energy levels and band gaps in the boron layers were determined at various times during this contractual effort by electrical as well as optical means. Curves of $\log I$ versus $1/T^{\circ}K$ were made at various times throughout the contract, particularly as the purity of the films improved. A stated purpose of this contract was to determine the electrical effects of impurity levels on amorphous materials. These measurements show that a band gap exists with impurity type levels in the gap very little different than that found in crystalline materials. Originally (Quarterly Report No. 5), shallow energy levels were observed at approximately 0.1 eV. Since these shallow levels were observed in amorphous materials by other workers, it was believed that this may be a property of the amorphous state and represented a mobility activation. As the samples became purer, however, this level disappeared. Currently, only one level seems to exist near the center of the band gap. This level behaves like a recombination level found in crystalline materials. Since measurements were not carried out at low temperature, it is, of course, possible that very shallow levels do exist.

2.2.4 Conduction Mechanism

The present experimental work indicates that the conduction mechanism in amorphous boron layers follows the same laws as that found in the crystalline materials. At low voltages, before space charge or avalanche sets in, the current is ohmic, the number of charge carriers is about that required by statistics and the

mobility is very low. Following this ohmic behavior, one has a space charge region exactly analogous to that found in high resistivity crystalline insulators or semiconductors. Mobility may be determined in this region (see appendix) and turns out to be $\sim 10^{-3} \text{ cm}^2/\text{V-sec}$ which seems to fit with all of the observed behavior. As far as is known, this is the first time that mobility has been measured for an amorphous layer of this type. A technique is thus available for observing very small mobilities in pure, thin amorphous layers.

There seems to be no evidence of impurity band conduction, hopping conduction, or mobility activation in the pure material. As the voltage is increased beyond the space-charged limited region, one observes avalanche and switching which is also observed in crystalline semiconductors. Whether the behavior observed here is carried over to other amorphous semiconductors is yet to be determined.

2.3 References

1. W. F. Zimmerman III, A. M. Murphy, and C. Feldman, Applied Physics Letters 10, 71, (1967).
2. For a review, see J. Tauc, "Progress in Semiconductors," Vol. 10 Edited by A. G. Gibson (1966).
- 3.(a) J. Tauc, A. Abrahám, L. Pajasová, R. Grigorovici, and A. Vancu, Proc. Conf. Physics of Non-Crystalline Solids, Delft-North Holland (1964).
- (b) J. Tauc, R. Grigorovici, and A. Vancu, Phys. Stat-Sol., 15, 627 (1966).
- (c) J. Tauc, R. Grigorovici, and A. Vancu, Proc. Int'l. Conf. Physics of Semiconductors, Kyoto (1966) Supplement, J. Phys. Soc. Japan 21, 123 (1966).
4. A. H. Clark, Phys. Rev. 154, 750 (1967).
5. M. Cardona and G. Harbeke, J. Appl. Phys. 34, 813 (1963).
6. P. M. Grant and W. Paul, J. Appl. Phys. 37, 3110 (1966).
7. H. R. Phillip and E. A. Taft, Phys. Rev. 113, 1002 (1959), ibid 120, 37 (1960).
8. Sh. Z. Dhamagidze, R. R. Shavangiradze, Yu. A. Mal'tsvev, and F. M. Gvilava, Fizika Tverdogo Tela 7, 1563 (1965) [English translation: Soviet Physics - Solid State 7, 1259 (1965)]. References to earlier work are contained in this article.

9. Proc. Int'l. Symposium on Boron (Paris, 1964 - Plenum Press, N. Y. 1965).
10. J. Stuke (To be published 1967) as quoted in N. F. Mott, Adv. in Physics, 16, 49 (1967).
11. F. Ordway (to be published) - 8th Quarterly Report.
12. H. Richter and G. Breitling, Z. Naturf 13a 988 (1958).
13. L. Banyai, Proc. Int'l. Conf. Physics of Semiconductors, Paris (1964; Dunod).
14. R. Grigorovici, N. Croitoru, N. Dévényi and E. Teleman, Proc. Int'l. Conf. Physics of Semiconductors, Paris (1964; Dunod).
15. D. Beaglehole, Phys. Rev. Letters 15, 551 (1965).
16. H. R. Phillip, Solid St. Comm. 4, 73 (1966).
17. G. Baldini, Phys. Rev. 128, 1562 (1962). J.-Y. Roncin, V. Chandrasekharan, and N. Demany, Compt. Rend. 258, 2513 (1964).
18. J.-Y. Roncin and K. Moorjani (to be published, Phys. Stat. Sol.) Sept. 1967.

3. PUBLICATIONS

During the course of this contract, a number of publications have appeared as the work progressed; these include the following:

- a. "Electrical Properties of Amorphous Semiconductors," Kishin Moorjani and Charles Feldman, Reviews of Modern Physics, Vol. 36, No. 4, pp 1042-1049, 1964.
- b. "Vacuum Deposited Amorphous Boron Films," Charles Feldman, Fred Ordway, William Zimmerman III, and Kishin Moorjani, in "Boron Vol. 2 - Preparation, Properties, and Applications," Ed. G. K. Gaule, Plenum Press, New York (1965) pp 235-260.
- c. "Infrared Absorption in High-Purity Boron Films," William Zimmerman III, Anne M. Murphy, and Charles Feldman, Applied Physics Letters, Vol. 10, No. 3, pp 71-73 (1967).
- d. "Dispersion of Amorphous Boron Films in the Near Infrared," Anne M. Murphy, Journal American Optical Society, Vol. 57, No. 6, 845 (1967).
- e. "Switching and Negative Resistance in Amorphous Boron Layers," Charles Feldman and William A. Gutierrez, to be published. (Appendix).

4. PERSONNEL

The following personnel have contributed to the progress of this program either directly or indirectly:

Dr. Charles Feldman

William A. Gutierrez

Kenneth G. Hoggarth

Miss Anne M. Murphy

Dr. Kishin Moorjani

Dr. Fred Ordway

William Zimmerman III

5. SUMMARY

It becomes extremely difficult to summarize a 3-year effort in a few short paragraphs. In the study of amorphous semiconductors, it is apparent that this program has only scratched the surface and that a great deal more work must be done before a complete understanding of the relation between amorphous and crystalline materials may be reached.

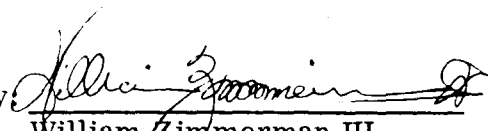
It has been shown that there appear to be certain optical and electrical properties of amorphous thin films which are characteristic of several different materials. It has further been shown that certain characteristics of crystalline thin films agree with those of single crystal bulk material. It is thus possible to expect that the properties of amorphous thin films would be in good agreement with the similar properties in bulk amorphous materials.

The optical study of boron films has failed to show any noticeable structure out as far as 9.0 eV. The absorption has just continued to rise. It has been demonstrated that, at least in the near infrared, impurity levels are optically active. It has also been concluded that there is not much modification in the band structure between crystalline and amorphous boron and germanium.

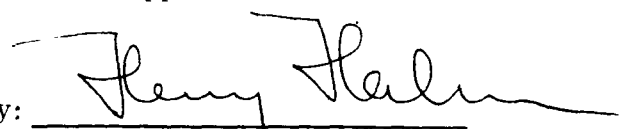
In the electrical studies, it has been shown that boron, together with a number of other semiconductor materials, shows a number of different conduction mechanisms but that these are similar to crystalline materials. As voltage increases, these go from ohmic to space-charge limited to avalanche conduction mechanisms before switching occurs.

In conclusion, it is strongly recommended that further work on the characteristics of amorphous semiconductors be carried out, with emphasis on the relationship between amorphous and crystalline properties. A much wider range of materials must be examined in order to permit the characterization of amorphous materials and the development of new theories or confirmation of existing theories of amorphous semiconduction.

Prepared by:


William Zimmerman III
Head, Materials Development
and Applications

Approved by:


Henry Hahn
Manager, Materials Laboratory

APPENDIX

SWITCHING AND NEGATIVE RESISTANCE IN AMORPHOUS BORON LAYERS*

Charles Feldman⁺ and William A. Gutierrez

Physical Electronics Laboratory
Melpar, Inc.
Falls Church, Va. 22046

Reversible, current controlled, negative resistance and switching has been observed in a variety of polycrystalline and amorphous thin films.¹ As far as is known, no completely satisfactory explanation of the phenomena has been postulated. In this communication, observations on switching in amorphous boron films are described and an explanation of the behavior is suggested which is somewhat different from other proposed explanations.

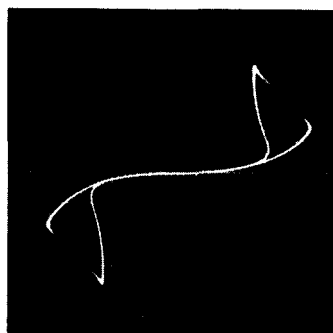
The observations follow from previous studies of amorphous boron layers in which charge multiplication was directly observed in aluminum electroded samples.^{2,3} In the present study titanium electrodes were used, no forming procedure was required, and the current was directly proportional to the electrode area (i. e. , no breakdown in localized spots).

The samples were deposited from pure boron by electron bombardment in a manner previously described.³ Residual gas analysis during deposition and IR transmission measurements, following deposition, were used as an aid in achieving boron film purity.⁴ Titanium was deposited from tungsten boats by resistance heating. Samples were made without opening the vacuum chamber as well as in separate chambers — one for titanium and one for boron. Most consistent results were obtained when the samples were made without breaking the vacuum and these are the results reported here.

Figure A-1 shows the room temperature, current (I) - voltage (V), characteristic of a typical sample. The characteristics are approximately symmetrical about the origin. A log-log plot of the trace is shown in figure A-2. The current is at first ohmic, then changes to a V^2 dependency, typical of single carrier, space-charge-limited currents, and finally, just before switching, follows a V^n relation where n is

*This work was supported in part by the Naval Air Systems Command, Department of the Navy, and the National Aeronautics and Space Administration.

⁺Now at Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Md.



SCALE: VERTICAL - 1 ma/div
HORIZONTAL - 1 VOLT/DIV
($R_{LOAD} = 1 \text{ KOHM}$)

Figure A-1. Oscilloscope Display of the Room Temperature I-V Characteristic of a Boron Sample No. 536 Area 10^{-4} cm^2 Thickness 3000 AU. (Vertical: 1 mA/Div., Horizontal: 1 V/Div., Load: 1 K)

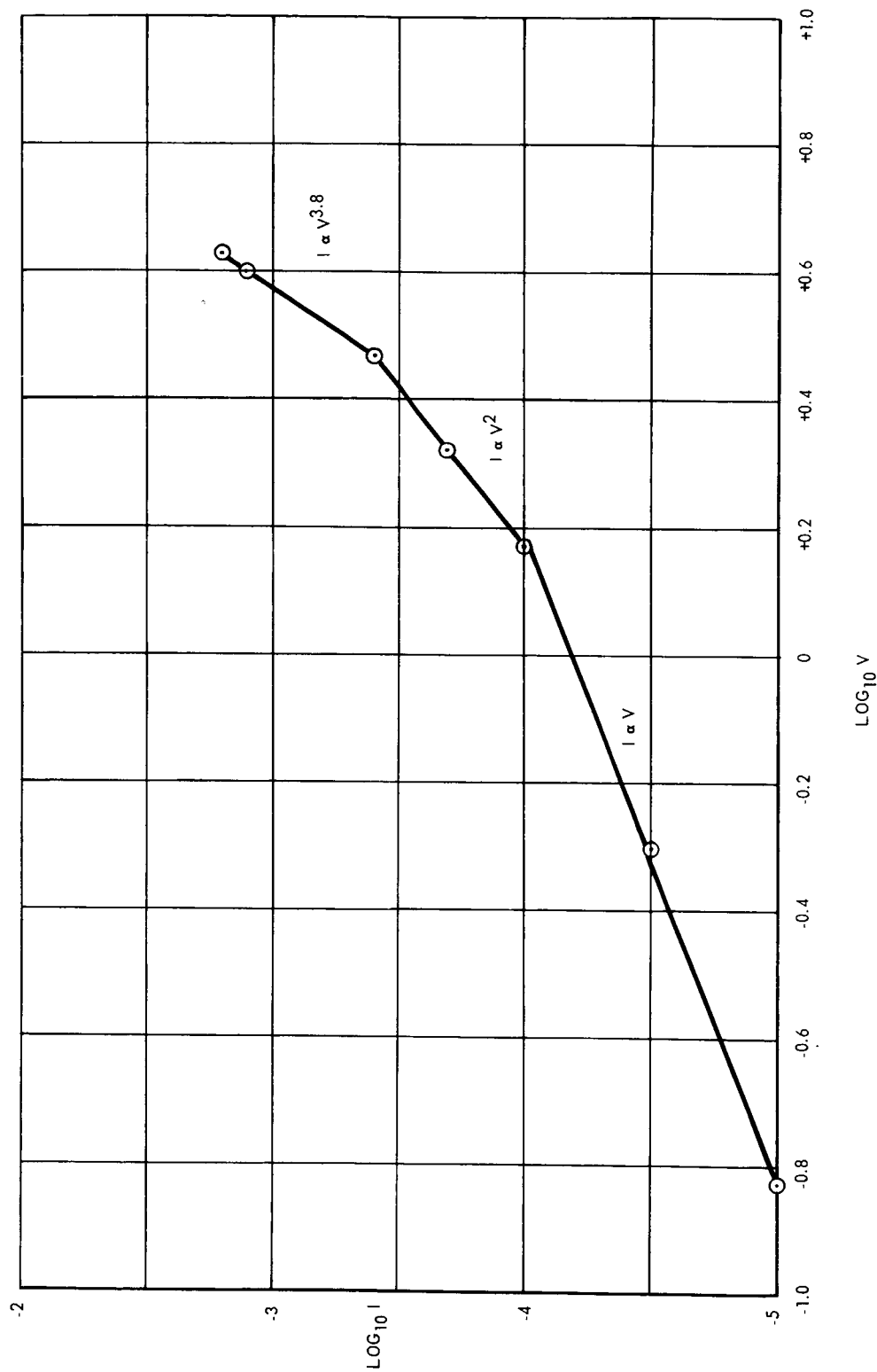


Figure A-2. Log I vs. Log V Plot of the Trace Shown in Figure A-1

greater than 3. The transition from the high to the low-impedance state is load dependent, and the resistance of the low-impedance state appears limited only by the electrode resistance. Increasing the current further in the low-impedance region leads to irreversible breakdown. A second space-charge region ($I \propto V^2$) in this low-impedance state has not been observed.

Plots of $\log I$ vs. $1/T^\circ K$ at any point below the switching region reveal two definite slopes, S_1 and S_2 , which may be interpreted as a band gap $\Delta E_g \propto 2S_1$ and a level $\Delta E_r \propto 2S_2$. Efforts to find an effect of light on the switching properties by exposure to various sources have not been successful.

Typical sample parameters are listed table A-1. The pertinent facts revealed in this table are:

- a. The threshold voltage (V_{th}) and sustaining voltage, V_s are independent of sample thickness.
- b. The ratio of V_{th}/V_s is equal to the ratio $\Delta E_g/\Delta E_r$.
- c. The thicker the boron film the greater the current density (J) for a fixed value of the electric field.

A plot of $\log J$ vs. film thickness (d) for a fixed field in the $I \propto V^n$ region is given in figure A-3. To obtain the same field for each sample, values were calculated using the approximately observed value of $n = 4$. Assuming avalanche ionization, a value of ionization coefficient, α , defined from $I = I_0 \exp(\alpha d)$ may be calculated from figure A-3. This yields a value of $\alpha \sim 2 \times 10^5 \text{ cm}^{-1}$ which is in reasonable agreement with the previously measured values.³

The various theories postulated to account for negative resistance do not seem entirely tenable in the light of the experimental evidence presented here. The lack of a dependency of threshold voltage on thickness and the symmetry in the I-V characteristics at low voltage seem to eliminate the double injection theory of Lampert.⁵ Vul et al.⁶ and Patil et al.⁷ have also observed the lack of threshold voltage dependence on thickness in thin samples. A space-charge-limited current following the switching to the low-impedance region predicted by Lampert has also not been observed. The filamentary injection theory of Barnett and Milnes⁸ is not applicable, since current-area relationships indicate that the effect occurs over the entire area. Theories based on recombination radiation or optical feedback effects,⁹ although tempting, cannot be justified at present. Theories based on rapid heating effects^{10, 11} do not seem valid because measurements at liquid nitrogen temperatures showed little change in the threshold and saturation voltage. Explanations based on direct impact ionization of shallow filled levels, which may lead to negative resistance according to McWhorter,¹² are not applicable because there is no evidence of the required levels.

TABLE A-1

SAMPLE PARAMETERS

Sample Number	Threshold Voltage V_{th} (volts)	Sustaining Voltage V_s (volts)	ΔE_g (eV)	ΔE_r (eV)	V_{th}/V_s	$\Delta E_g/E_r$	Thickness d (\AA)	Current Density at 2.7×10^5 V/cm J (amps/cm)
660	4.06	2.40	0.92	0.53	1.69	1.73	535	1.7×10^{-2}
658	4.52	2.62	0.78	0.43	1.73	1.81	1650	4.8×10^1
688	3.92	2.04	0.90	0.48	1.93	1.87	1900	7.8×10^1
740	4.03	2.09	0.84	0.44	1.93	1.91	1900	8.4×10^1
741	5.18	2.77	1.01	0.56	1.87	1.81	2000	9.2×10^1
681	4.80	2.20	0.96	0.45	2.18	2.13	2200	1.2×10^2
679	4.37	2.46	0.73	0.42	1.78	1.74	2675	2.3×10^3
536	4.40	2.40	0.95	0.51	1.86	1.83	3000	3.0×10^3
663	5.60	2.50	0.99	0.43	2.24	2.30	3300	3.4×10^3
770	6.15	2.60	1.00	0.43	2.36	2.33	6200	6.5×10^4
770	7.16	2.58	1.15	0.41	2.77	2.80	6420	1.5×10^4
770	5.72	2.70	0.99	0.47	2.12	2.11	6955	6.8×10^5
772	3.82	1.72	0.80	0.37	2.22	2.16	9000	1.4×10^6

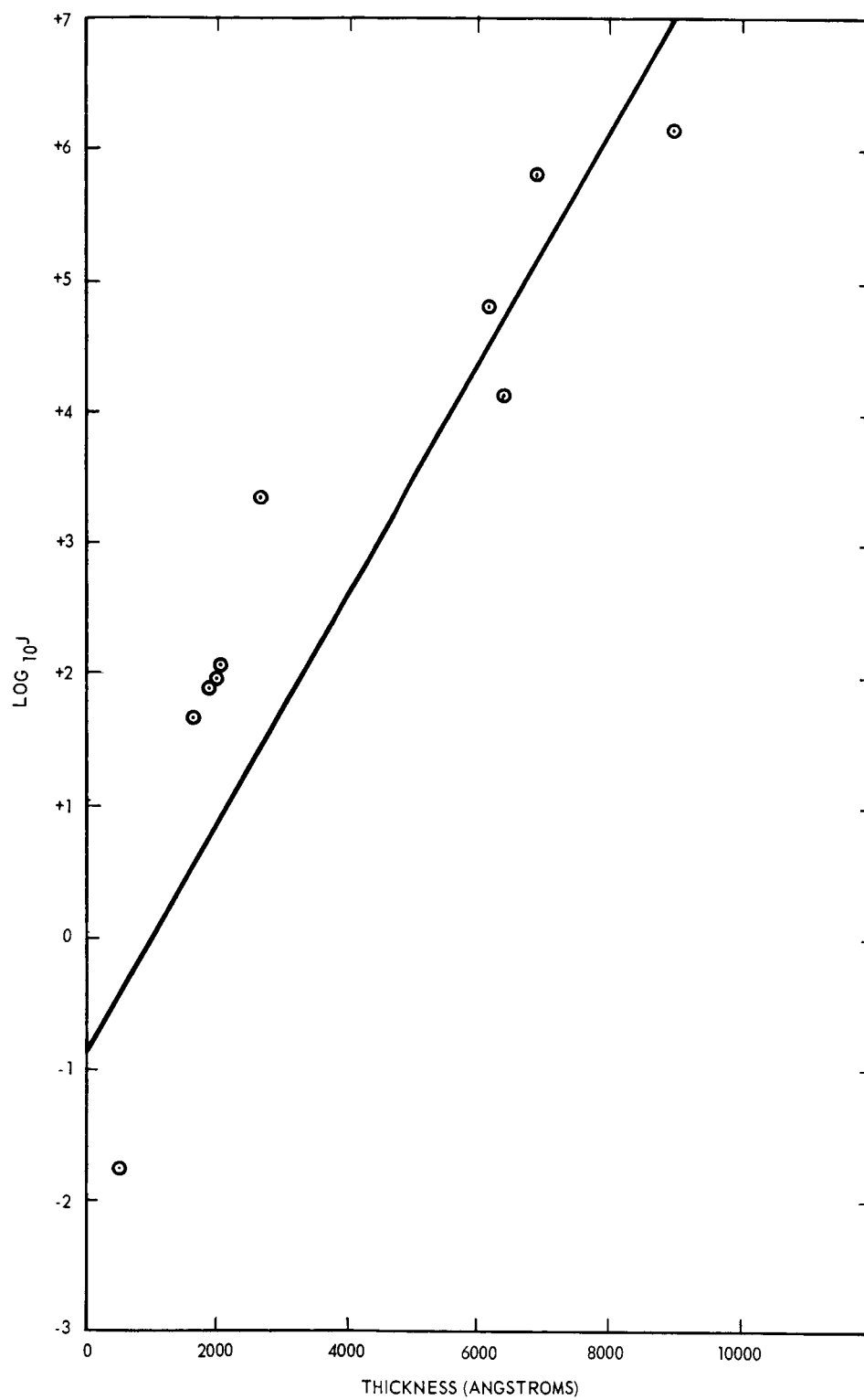


Figure A-3. $\text{Log } J$ vs. Film Thickness (d) for an Electric Field,
 $E = 2.7 \times 10^5 \text{ V/cm}$

The evidence of charge multiplication, the existence of an energy level in about the band center, and the consistent ratio between transition voltages and energy levels leads one to postulate a model based on a change in electron capture cross-section due to the filling with electrons of a recombination level by avalanche ionization. The role of a recombination level in the switching mechanism is described by both Lampert⁵ and Stafeev.¹² However, neither has postulated the particular mechanism of filling the level envisioned here.

The energy level scheme for the process is shown in figure A-4. The band edges are shown sharp for clarity, although it is possible that the edges in amorphous materials are less sharp than in single crystals. The sample is initially p-type with a recombination level, near the center of the forbidden band, filled with holes and void of electrons. The Fermi level is thus between this recombination level and the valance band. As the field increases, impact ionization in the valance band creates hole-electron pairs. (Impact ionization of electrons does not occur at the recombination level because it is void of electrons.) At this stage, the electrons in the conduction band recombine at the recombination centers, while the holes take part in the conduction process (V^n region). At the switching threshold voltage, the rate of increase of electrons in the conduction band becomes larger than the rate of recombination. (The quasi-Fermi level moves to a position approximately in the center of the band, since the number of holes is approximately equal to the number of electrons (figure A-4b).) The recombination centers are emptied of holes and the capture cross-section for electrons in the conduction band decreases. Electrons, as well as holes, now take part in the conduction process. Carriers may be supplied both by the electrodes and through continual impact ionization. Impact ionization in the valance band continues, but enough energy need only be supplied to keep the recombination states empty of holes. Since the recombination level is kept empty by the same collision mechanism that created the original hole-electron pairs, the ratio of threshold voltage to sustaining voltage is expected to be equal to the ratio of the band gap to the recombination level.

An assumption is made in this explanation that the electron transit time is smaller than the post-switched recombination time (τ_r), i. e. :

$$d^2/\mu_e V_{th} < \tau_r$$

This transit time may be roughly estimated by assuming that the hole and electron mobilities are equal in the high-conducting state and that the hole mobility is about the same as that found in the space-charge-limited region. Assuming a trap-free condition in the V^2 region, one may obtain the mobility from⁵

$$\mu_h = \frac{8 I d^3}{9 A \epsilon V^2}$$

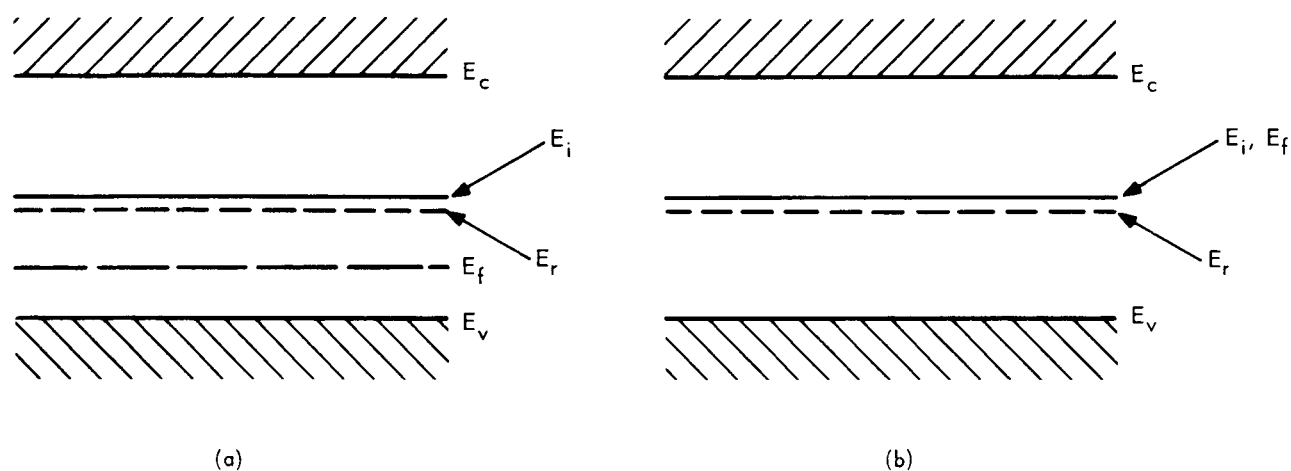


Figure A-4. Suggested Energy Level Scheme for Boron Films.
 (a) Before Switching, (b) After Switching E_r Recombination Level; E_f Fermi Level; E_i Intrinsic Band Center; E_c Conductor Band; E_v Valance Band

Using the dielectric constant $\epsilon = 9$, obtained from the IR refractive index,¹³ one obtains $\mu_h = 8 \times 10^{-3} \text{ cm}^2/\text{V-sec}$ for sample No. 536. This gives a transit time of about $2 \times 10^{-8} \text{ sec}$ which is a reasonable value for the suggested process. Switching of this type is thus not to be expected in very thick, low mobility samples. It is hoped to present a more complete treatment of this process in the near future.

The authors appreciate the efforts of Mr. Kenneth Hoggarth in preparing the samples.

REFERENCES

1. See for example:
K. L. Chopra, J. Appl. Phys., 36 184 (1965).
T. W. Hickmott, J. Appl. Phys., 35, 2679 (1964).
Y. Mizuchima, Y. Igarashi, O. Ochi, Proc. IEEE., 53, 322 (1965).
2. C. Feldman, Nature, 203, 964 (1964).
3. C. Feldman, F. Ordway, W. Zimmerman III, and K. Moorjani, Boron (Plenum Press, New York, 1965), Vol. 2, pp. 235-259.
4. W. Zimmerman III, A. M. Murphy, C. Feldman, Appl. Phys. Ltrs., 10, 71 (1967).
5. M. A. Lampert, Phys. Rev., 125, 126 (1962).
6. B. M. Vul, E. I. Zavaritskaya, and I. V. Davydova, Soviet Phys. -Solid State, 5, 808 (1963).
7. S. G. Patil, A. P. B. Sinha, Brit. J. Appl. Phys., 18, 361 (1967)
8. A. M. Barnett and A. G. Milnes, J. Appl. Phys., 37, 4215 (1966).
9. W. P. Dumke, Physics of Semiconductors-Proceedings of 7th International Conference, Paris 1964. Academic Press, New York, p. 611.
10. W. Dietz and H. Helmberger, Boron (Plenum Press, New York, 1965), Vol. 2, pp. 301-316.
11. A. L. McWhorter and R. H. Rediker, Proc. IRE, 47, 1207 (1959).
12. V. I. Stafeev, Soviet Phys. -Solid State, 1, 763 (1959).
13. A. M. Murphy, J. Opt. Soc. Am., 57, 845 (1967).